

CONTROL OF MERCURY EMISSIONS IN FLUE GASES BY ACTIVATED CARBON ADSORPTION

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ABSTRACT

The adsorptive capacities of virgin and sulfur impregnated activated carbons (GAC) for gas-phase mercury were evaluated as a function of temperature and influent mercury concentration. The virgin activated carbon showed little adsorptive capacity, especially at temperatures above 90 °C. The pronounced effect of temperature on the adsorptive capacity evidences a physical adsorption mechanism between the mercury and virgin GAC. Sulfur impregnated activated carbons exhibited enhanced mercury removal efficiency over the non-impregnated varieties due to formation of mercuric sulfide on the carbon surface. This chemisorption process is enhanced with increased temperature between 25 and 90 °C. However, at 140 °C a decrease in adsorptive capacity occurs, indicating reduced formation of mercuric sulfide. The method used for impregnating GAC with sulfur had a pronounced effect on mercury removal capacity. The chemical bonding of sulfur and carbon surface at 600 °C provides a more uniform distribution of sulfur throughout the GAC pore structure than achieved by conventional condensation techniques, yielding improved performance.

INTRODUCTION

Numerous studies have documented the pathways of trace contaminants through coal-fired power plants⁽¹⁻⁴⁾. Lack of mass closure for Hg, Se, Cl, and Br indicates that these elements exist entirely in the gas phase upon exiting the combustion zone, and pass unaffected to the smokestack⁽¹⁾. Numerous studies have shown that the best available control technology for particulate pollution abatement (high-efficiency electrostatic precipitator) has virtually no impact on the release of vapor-phase trace elements to the atmosphere^(1,3-5). The estimated quantity of mercury released globally from coal combustion is 3000 metric tons per year⁽⁵⁾. Gaseous mercury emissions exist in both the elemental and oxidized (Hg²⁺) forms. Chu and Schmidt⁽⁶⁾ have determined that the percent of oxidized mercury in flue gases is a function of the coal type and composition. By quantifying the speciation of mercury in flue gases Prestbo and Bloom⁽⁷⁾ reported that particulate forms of mercury generally constitute less than 5% of the total mass of mercury emitted.

The deposition of mercury following discharge to the atmosphere causes some local, but mostly regional impacts. Klein and Russel⁽⁸⁾ showed that the soil around a Michigan power plant was enriched with Cd, Co, Cr, Hg and Ni, with contaminant concentration gradients reflecting the prevailing wind patterns. Hall et al.⁽⁹⁾ found that the elemental Hg⁰ will add to the atmospheric background concentration, while the divalent gaseous and particle-associated mercury will have a tendency to deposit within the region where it is emitted.

Increased levels of mercury in the environment are of particular concern due to well documented food chain transport and bioaccumulation of mercury and its forms⁽¹⁰⁾. Mercury is highly toxic to algae, fungi and seed plants. Mercury tends to accumulate in the lower stem areas rather than in the upper photosynthetic areas. Mercury is a cumulative poison in animals since there is no known homeostatic mechanism for regulating mercury concentration in tissues. Mercury is also a potent neurotoxin that is capable of causing irreversible damage to the central nervous system, or even death. Metabolism and degree of toxicity of mercury to animals is a function of several factors: chemical form, route of entry, duration of exposure, and dietary content of interacting elements, especially selenium. Mercury vapors can cause bronchitis, interstitial pneumonia, circulatory collapse, renal failure and dermatitis, while mercury salts can cause anorexia, memory loss, weight loss and gingivitis. Methylmercury causes paresthesia, hearing loss, ataxia, peripheral vision loss and cerebral disease⁽¹¹⁾.

Regulatory initiatives and increased public concern regarding elevated levels of mercury in the environment have stimulated research efforts to develop technologies for mercury emission control. Although there are currently no regulations for mercury emissions from electric utilities, the Clean Air Act Amendments of 1990 (Title III, Section 112[b][1]) (CAAA) require major sources to use the best available control technology (BACT), and require the U.S. Environmental Agency (EPA) to perform a study of mercury emissions.

Activated carbon adsorption is a technology that offers great potential for the control of gas-phase mercury emissions. Sinha and Walker⁽¹²⁾ demonstrated that the capacity of sulfur impregnated carbons greatly surpassed the virgin carbons at 150 °C due to chemical adsorption of mercury

(through formation of mercuric sulfide) on the carbon surface. Matsumura⁽¹³⁾ found that iodized and oxidized activated carbons adsorb 20-160 times more mercury than the untreated variety. Metzger and Braun⁽¹⁵⁾ determined that 5% iodine impregnated activated carbon was an excellent adsorbent for elemental mercury, with the adsorptive capacity greater than 5 mg/g at temperatures ranging from 20 to 180 °C. Otani et al.⁽¹⁴⁾ found that increased sulfur impregnation up to 13.1 wt. %, did not have a detrimental effect on elemental mercury adsorption at low temperatures (36 °C), as reported by Sinha and Walker⁽¹²⁾. Otani et al.⁽¹⁴⁾ suggested that the contradicting results are related to surface area reduction resulting from different impregnation methods and activated carbon types. They also found that a portion of the sulfur impregnated on the activated carbon surface is chemically adsorbed, and not available to react with mercury to form mercuric sulfide. Krishnan et al.⁽¹⁵⁾ demonstrated that the virgin activated carbons adsorbed less mercury with increased temperature, and that heat pretreatment with clean nitrogen at 140 °C destroyed active sites, reducing the adsorptive capacity further still. Livengood et al.⁽¹⁶⁾ showed that the adsorption capacity of sulfur impregnated carbon decreased with an increase in temperature from 55 to 90 °C.

MATERIALS AND METHODS

Three types of activated carbons were used in this study. Two of the carbons, Filtrasorb-400 (F-400) and HGR were supplied by the manufacturer (Calgon Carbon Corporation, Pittsburgh, PA) in 12x40 and 8x12 U.S. Mesh sizes, respectively. The third type, F-400S, was produced by contacting F-400 carbon with excess amount of sulfur in a pure nitrogen atmosphere at 600 °C. The sulfur contents of F-400, F-400S, and HGR were 0.76, 7.61, and 9.24 wt. %, respectively. The particle size used in this study was 60x80 U.S. Mesh size.

A schematic representation of the experimental setup is shown as Figure 1. By varying temperature of mercury permeation cell and nitrogen flow rate, a wide range of mercury concentrations were generated. The impinger solution used for absorbing gas-phase mercury was prepared with 1.5% potassium permanganate in 10% sulfuric acid as described by Shendrikar et al.⁽¹⁷⁾ Quantification of elemental mercury in the gas phase was performed at a wavelength of 253.7 nm using a Perkin-Elmer Model 403 atomic absorption spectrophotometer (AAS) (Perkin-Elmer, Norwalk, CT) fitted with 18-cm hollow quartz gas cell (Varian Australia Pty. Ltd., Mulgrave, Victoria, Australia). Vapor-phase mercury detection limit for the analytical system used in this study was 1.8 µg/m³.

Breakthrough curves were generated using a 3/16 inch stainless steel column charged with 100 mg of activated carbon. The bed was secured in the adsorber by two 200 U.S. Mesh size stainless steel screens. The adsorber was operated in the downflow mode to minimize the potential for fluidization of the packed bed. The influent gas and activated carbon temperatures were regulated by placing the adsorber in a temperature controlled oven. With both the mercury generation device and adsorber off-line, clean nitrogen was passed through the AAS cell for 30 minute warm-up period. Once the lamp output was stabilized and AAS zeroed, the mercury generation device was placed on-line, and the oil bath temperature adjusted to generate the desired mercury concentration. The gas flow rate was adjusted to 0.97 L/min and the absorbance from the AAS was recorded following a 2 hour equilibration period. The adsorber was then placed on-line and the effluent mercury concentrations were continuously monitored until complete breakthrough. Several blank runs with no carbon in the adsorber that were performed at temperatures ranging from 25 -140 °C using an influent mercury concentrations in the range of 25-115 µg/m³ revealed that no uptake or transformation of elemental mercury was facilitated by the stainless steel reactor or support screens.

RESULTS AND DISCUSSION

Figure 2 summarizes the adsorptive capacities measured for F-400 activated carbon at different temperatures. The increase in the slope of the isotherm lines with an increase in temperature shows that bonding of mercury to the carbon surface decreases with an increase in temperature. Only a single data point is shown at 200 °C because no adsorptive capacity was detected at the next lower influent concentration increment of 55 µg/m³. The pronounced effect of temperature on the adsorptive capacity of F-400 GAC for elemental mercury indicates that the adsorption mechanism is physical in nature.

A series of experiments was conducted to determine the adsorptive capacity of sulfur impregnated (HGR) activated carbon as a function of adsorber temperature. The influent mercury concentration was maintained at 55 µg/m³ in all cases while the adsorber temperature was 25, 50, 90, and 140 °C. Figure 3 indicates that the adsorptive capacity of HGR carbon for mercury increases with an increase in temperature. However, this figure accounts only for the elemental form of mercury in the adsorber effluent as detected by the AAS. A separate experiment was performed to simultaneously monitor the effluent from an adsorber maintained at 90 °C for elemental and total mercury. The elemental form (Hg⁰) was constantly monitored by AAS output, and the total mercury concentration was determined by trapping the gases in an impinger train at various time increments. As illustrated in Figure 4, complete breakthrough was achieved for total mercury, while

elemental mercury reached equilibrium effluent concentration at C/C_0 equal to 0.6. The difference is attributed to the presence of mercuric sulfide in the adsorber effluent. Once a critical concentration of mercuric sulfide is formed on the surface of the GAC, desorption of mercuric sulfide occurs, forcing the product (HgS) into the effluent gas stream with the desorption process being more pronounced at 90 °C than at 20 or 50 °C.

Figure 5 compares the breakthrough characteristics of HGR GAC at 25 and 140 °C. As is apparent from this figure, after 8 hours into the experiment, the effluent from the adsorber operated at 140 °C reached complete breakthrough, while the effluent from the adsorber operated at 25 °C reached equilibrium at C/C_0 equal to 0.75. Experimental investigations of sulfur loss from the carbon surface upon exposure to nitrogen gas at various temperatures revealed that the low adsorptive capacity of HGR GAC exhibited at 140 °C can not be the result of sulfur loss from the carbon surface. However, this difference in behavior may be attributed to the fact that both physisorption and reaction with sulfur contribute to mercury uptake at 25 °C while only the reaction with sulfur could be occurring at 140 °C. Another possible explanation for the observed behavior is that the rate of HgS formation on the surface of the sulfur impregnate is much higher at 140 than 25 °C so that the HgS would quickly blind the sulfur surface and prevent any further mercuric sulfide formation, which results in complete breakthrough.

Figure 6 compares the adsorptive characteristics of F-400S to that of HGR and F-400 at 25 °C and an influent mercury concentration of 115 $\mu g/m^3$. As is apparent from this figure, F-400S performed much better than HGR and F-400. The superior adsorptive capacity of F-400S over HGR can not be explained by sulfur content on the GAC surface since F-400S contained 7.61 wt. % sulfur while HGR contained 9.24 wt. % sulfur. It is hypothesized that the higher adsorptive capacity of F-400S is the result of improved sulfur distribution throughout GAC surface. The sulfur in the HGR pore is most likely deposited by condensation as a slug deeply imbedded in the pore. Since the sulfur in the case of F-400S carbon is chemically bonded to the surface, it is more evenly distributed over the entire surface area. Although HGR carbon has higher sulfur content as compared to F-400S, the mercury-sulfur reaction on the surface of the HGR carbon is limited by the rate of diffusion of mercuric sulfide from the surface into the sulfur mass.

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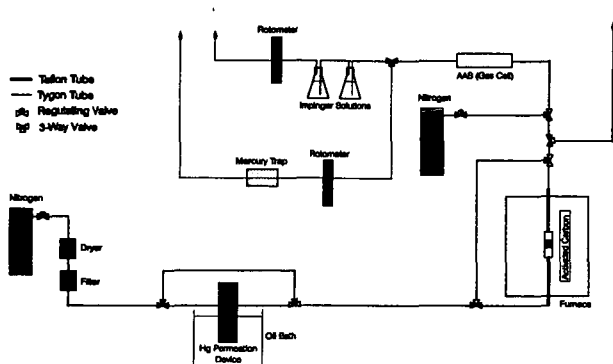


Figure 1. Schematic representation of the experimental system

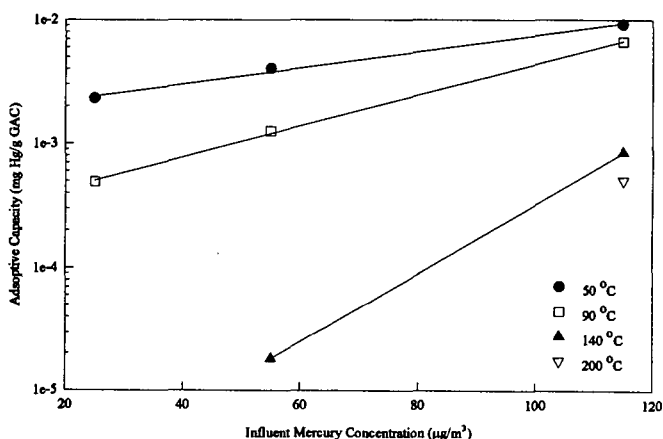


Figure 2. Adsorptive capacity of F-400 GAC for vapor-phase mercury

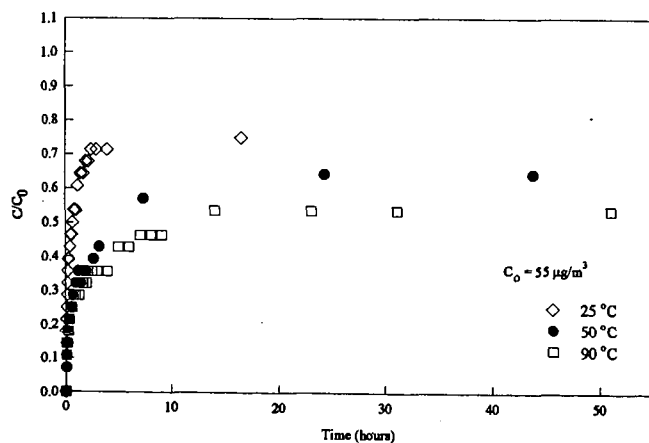


Figure 3. Effect of temperature on mercury breakthrough from HGR adsorber

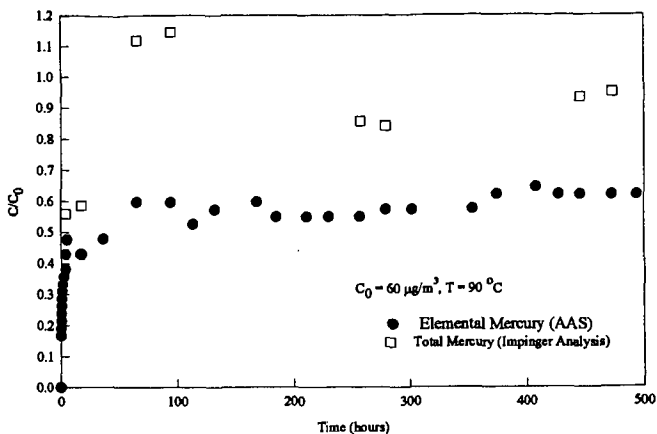


Figure 4. Elemental and total mercury breakthrough from HGR adsorber

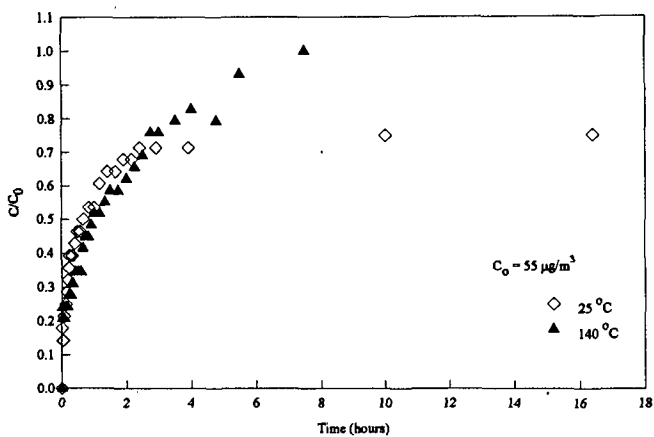


Figure 5. Breakthrough of mercury from HGR adsorber at 25 and 140°C

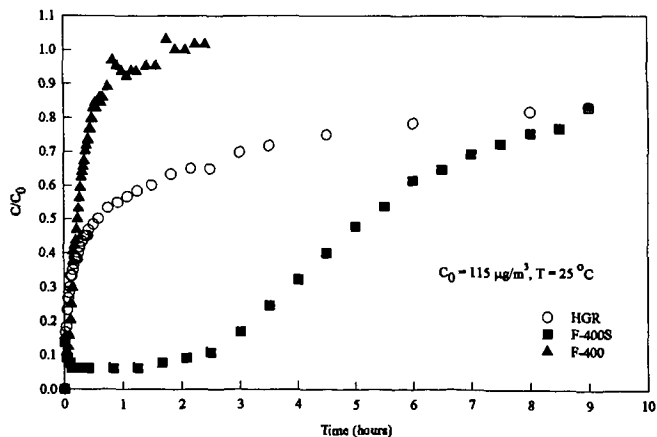


Figure 6. Removal of mercury by F-400, HGR and F-400S activated carbons